BAT421: 3D printing of solid-state Li batteries

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Overview:

Timeline: Nov. 2018 to Feb 2022. 80% completion

Budget: Total $1.125M FY21: $375K

Barriers: (Performance) The integration of ceramic solid state electrolyte into solid state batteries is challenging due to the brittleness, air-sensitivity, and poor solid-solid contact issues.

Partner: Simulation group led by Brandon C. Wood (LLNL) on "Integrated multiscale model for design of robust 3D solid-state lithium batteries"

Impact: Unlike the well-established roll-to-roll fabrication of conventional Li-ion batteries, the processing of SSBs is unique due to the brittleness of solid-state electrolytes (SSEs). Commercial SSE separators are ultrathick, which limits power and energy densities. Free-standing ultrathin ceramic separators are mechanically fragile.

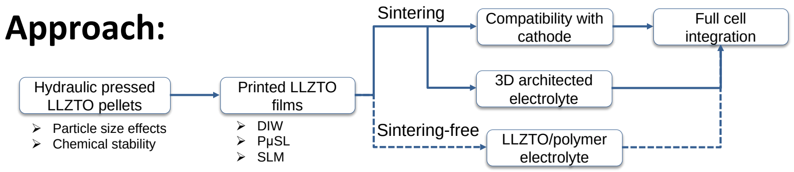
Strategies: 3D printing enables multi-component integration and interfacial engineering including morphological, chemical and mechanical control.

Objectives: 1) Tuning microstructures of 3D printed SSE separators. 2) Process compatibility with cathode printing. 3) 3D printing of sintering-free SSE separators.

FY21 Milestones:

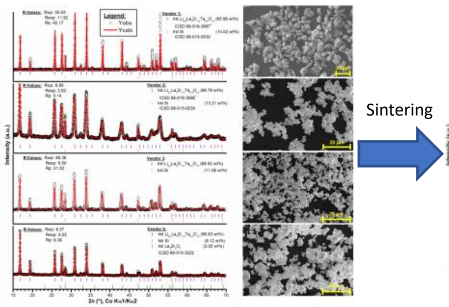
FY21Q1: Evaluation of new LLZTO feedstocks (complete)
FY21Q2: Battery performance based on 3D architected LLZTO (complete)
FY21Q3: Battery performance based on CPE (in progress)
FY21Q4: 3D SSB battery performance and failure mechanisms

Approach:

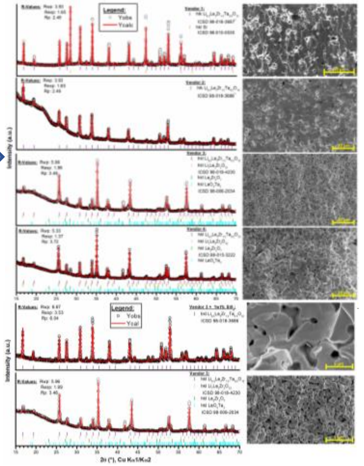


Accomplishment to date - FY21

- Evaluation of new LLZTO feedstocks. (Vendor 2 wins out)

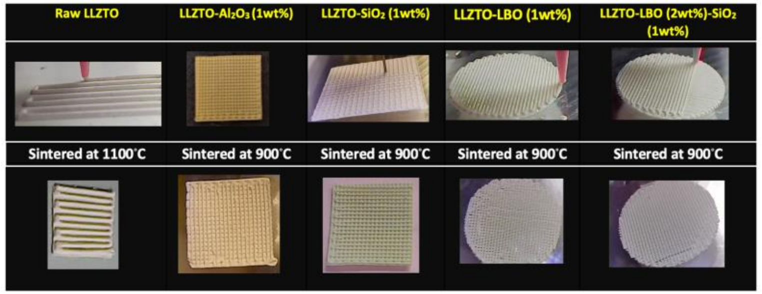


Manufacturer	ICP-OES analysis	Shrinkage (%) and Relative density (%) of sintered pellets @ 1100°C
Vendor 1	$Li_{7.10}La_{3.00}Zr_{1.39}Ta_{0.61}O_x$	~13% and 93%
Vendor 2	$Li_{6.84}La_{3.00}Zr_{1.38}Ta_{0.60}O_x$	31.02% and 92%
Vendor 3	$Li_{6.53}La_{3.00}Zr_{1.46}Ta_{0.50}O_x$	1.42% and 60%
Vendor 4	$Li_{6.26}La_{3.00}Zr_{1.53}Ta_{0.67}O_x$	2.49% and 75%

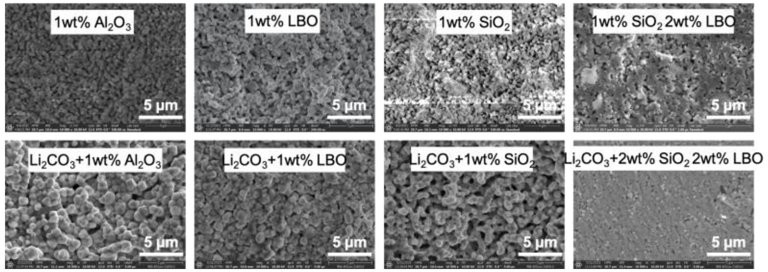


Addition of Li_2CO_3 + SiO_2 prevents the decomposition of vendor 3 powder.

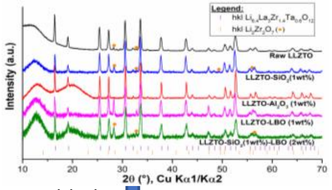
- 3D-printed LLZTO structures before and after sintering



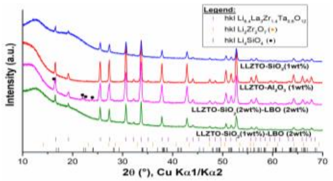
- Batter densification was achieved by the addition of Li_2CO_3.



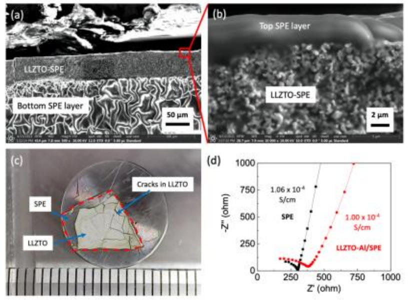
- LZO phase was prevented by adding Li_2CO_3 or Al_2O_3.



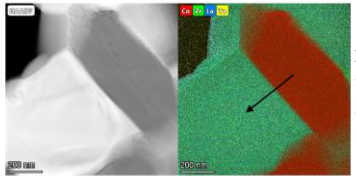
Li_2CO_3 added



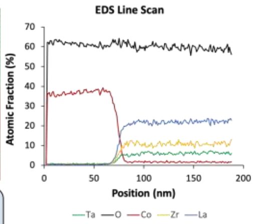
- Porous LLZTO film was infilled with SPE to enhance mechanical robustness, ionic conductivity, and contact with electrodes.



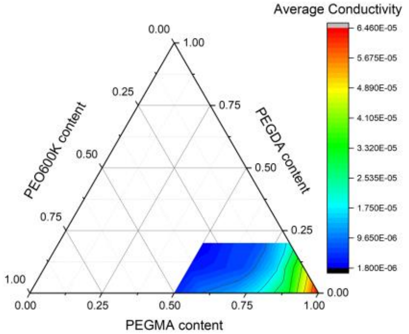
- Co-sintering stabilities.



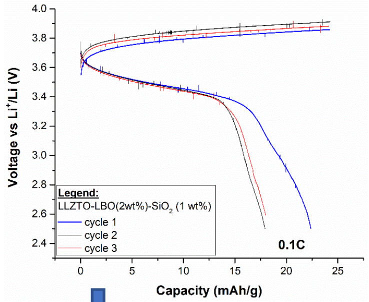
- Sintered pellet was made from LLZTO MTI BM/LCO BM powders BM 50/50 wt% 60 min; Sint. 900°C 2h air
- Clean interface between LLZTO and LCO—about 15-20 nm interfacial region



- PEGDA/PEGMA/PEO based solid polymer electrolytes were developed and tested at RT.



- First NMC/CPE/Li full cell



Possible issues

- PVDF may block porous channel in LLZTO separator
- SPE may not be in direct contact with NMC leading to higher interfacial impedance
- Impurity phase LLZTO reduces ionic conductivity
- PEO/PEG may not be stable enough against NMC
- Very high NMC loading (29 mg/cm²)